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This research project has successfully determined the reaction mechanisms for the pyrolysis of the group III precursors trimethylgallium (TMGa) and trimethylindium (TMIn) and the group V precursors AsH<sub>3</sub>, PH<sub>3</sub>, trimethylarsine (TMAs), dimethylarsine (DMAs), triethylarsine (TEAs), diethylarsine DEAs), monoethylarsine (MEAs), tertiarybutylarsine (TBAs), and tertiarybutylphosphine (TBP). The reaction mechanisms have also been studied for combinations of the group III and group V precursors which result in the production of GaAs and InP. The technique used is mass spectrometry with the pyrolysis occurring in various ambients including H<sub>2</sub>, He, and D<sub>2</sub>. The latter allows labelling of reaction products involving interaction with the ambient. The reaction mechanisms observed are surprisingly diverse. The pyrolysis temperatures for the various As precursors can be compared.

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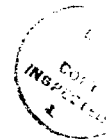
USE OF D<sub>2</sub> TO ELUCIDATE OMVPE GROWTH  
MECHANISMS

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## SUMMARY

This research project has successfully determined the reaction mechanisms for the pyrolysis of the group III precursors trimethylgallium (TMGa) and trimethylindium (TMIn) and the group V precursors AsH<sub>3</sub>, PH<sub>3</sub>, trimethylarsine (TMAs), dimethylarsine (DMAs), triethylarsine (TEAs), diethylarsine (DEAs), monoethylarsine (MEAs), tertiarybutylarsine (TBAs), and tertiarybutylphosphine (TBP). The reaction mechanisms have also been studied for combinations of the group III and group V precursors which result in the production of GaAs and InP. This report briefly summarizes the body of information generated during the 3 years since the inception of the project. It emphasizes research carried out during the third year of this project, which has concentrated on the determination of the pyrolysis mechanisms of TMAs, DMAs, TEAs, DEAs, and MEAs, and their reactions with TMGa to form GaAs.

The technique used is mass spectrometry with the pyrolysis occurring in various ambients including H<sub>2</sub>, He, and D<sub>2</sub>. The latter allows labelling of reaction products involving interactions with the ambient. This year we have also added the new tool of adding methyl or ethyl radicals via the pyrolysis of the azo compounds azomethane and azoethane, which pyrolyze at low temperatures, producing N<sub>2</sub> and either methyl or ethyl radicals.

The reaction mechanisms observed are surprisingly diverse. For the similar molecules TMAs and DMAs, the pyrolysis routes are different. The former pyrolyzes via a hydrogenolysis reaction in an H<sub>2</sub> ambient while DMAs pyrolyzes via a complex radical process including attack of the parent molecule by methyl radicals produced via homolysis of the DMAs. For all three ethylarsine compounds radical reactions dominate the pyrolysis process. For TEAs, the radical processes occur by reactions between the ethyl radicals produced homolytically with the H<sub>2</sub> (or D<sub>2</sub>) ambient. The resultant H (or D) radicals attack the parent molecule, accelerating the pyrolysis process. For the two molecules DEAs and MEAs, both of which have H bonded directly to the As, the ethyl radicals react with the parent molecule directly by abstracting these H atoms. Because MEAs has two such H atoms, the abstraction reaction is more rapid, thus more dominant.

The pyrolysis temperatures for the various As precursors can be compared. As expected from bond strength arguments, the pyrolysis process is slowest for AsH<sub>3</sub> and most rapid for TBAs. The temperature difference for the conditions used is 250°C. The methyl arsenic precursors are slightly less stable than AsH<sub>3</sub>. Since radical reactions are unimportant for TMAs, the pyrolysis temperature is only about 50°C lower than for AsH<sub>3</sub>. However, the pyrolysis temperature of DMAs is

considerably (100°C) lower, due to the radical processes involved. For the ethylarsines, the pyrolysis temperatures are lower than for the equivalent methyl arsine compounds. Due to the lack of a direct attack of the parent molecule by the ethyl radicals, the pyrolysis temperature of TEAs is 50°C higher than for DEAs and MEAs, which have nearly equal pyrolysis temperatures.

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### APPENDIX A: REPRINTS AND PREPRINTS OF PAPERS RESULTING FROM AFOSR SUPPORT SUBMITTED DURING THE LAST 12 MONTHS.

1. Dimethylarsine: Pyrolysis Mechanisms and Use for OMVPE Growth, (with S.H. Li, C.A. Larsen, C.H. Chen, and D.W. Brown), J. Electron. Mater. 19 299 (1990).
2. Alternate Sources and Growth Chemistry for OMVPE and CBE Processes, J. Crystal Growth (Invited Paper and International CBE Conference, to be published).
3. Decomposition Mechanisms of Trimethylantimony and Reactions with Trimethylindium (with C.A. Larsen and S.H. Li) J. Crystal Growth (submitted).
4. Comparative Pyrolysis Study of Ethylarsines (with S.H. Li and C.A. Larsen), J. Crystal Growth, Proceedings of ICMOVPE-5, (accepted).
5. Mechanistic Study of Organometallic Vapor Phase Epitaxy, Proceedings of 1st International Conference on Epitaxy (Invited Paper, to be published).
6. Monoethylarsine Pyrolysis Mechanisms: Alone and with Trimethylarsine, (with S.H. Li and C.A. Larsen), J. Crystal Growth (submitted)
7. Radical Reactions in Pyrolysis of Triethylarsine and Diethylarsine, (with S.H. Li and C.A. Larsen), J. Crystal Growth (submitted).

## I. INTRODUCTION

This three year research project has produced the first systematic study of the pyrolysis and growth reactions for the wide range of precursors used in atmospheric pressure OMVPE. Two major features of the results stand out: 1) the reaction mechanisms are more complex than originally anticipated, and 2) a true picture of the complex reactions occurring can only be obtained by examining the entire range of precursors in the same apparatus using similar conditions and techniques.

The complexity of the reaction mechanisms has necessitated the development and use of a number of techniques, including: 1) isotopic labelling of the parent molecules, 2) use of a  $D_2$  ambient to allow labelling of the reaction products, 3) removal of radicals from the system using either toluene or 1,4-cyclohexadiene, and 4) addition of radicals to the system using the azo compounds  $R_2N_2$ , which pyrolyze at low temperatures giving R radicals (either methyl, ethyl, or t-butyl) and inert  $N_2$ . By combining these tools, a reliable determination of the reaction mechanism can be made.

The first two annual reports described the pyrolysis mechanisms for the group III precursors trimethylgallium (TMGa) and trimethylindium (TMIn). Even for these molecules the pyrolysis reactions are more complex than initially thought. In an  $H_2$  ambient, both molecules produce H radicals via the reaction between the methyl radicals produced by homolytic fission and the ambient. The H radicals can, in turn, attack the parent molecules, thereby increasing the pyrolysis rate. Such radical chain reactions will be more important for atmospheric pressure reactors where the frequency of gas phase collisions is large, approximately  $10^9 \text{ sec}^{-1}$ . Radical studies also show a slow reaction, unimportant in the  $H_2$  ambient, where  $CH_3$  radicals can directly attack the parent molecule. The addition of  $AsH_3$  assists TMGa pyrolysis, which is interpreted in terms of heterogeneous  $AsH_3$  attack of TMGa, perhaps via formation of an adduct on the surface.

The first two annual reports also deal with the group V precursors  $AsH_3$ ,  $PH_3$ , tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP). The hydrides pyrolyze completely heterogeneously via the sequential release of H atoms. The pyrolysis reactions for TBAs and TBP show how complex the chemistry can be. Apparently, 3 possible pyrolysis reactions are available: 1) A chain reaction can occur beginning with homolysis, producing  $AsH_2$  or  $PH_2$  and t-butyl radicals. The experimental evidence clearly shows that the t-butyl radicals attack the parent molecule, abstracting an H atom to form  $C_4H_{10}$ . 2) A  $\beta$ -elimination reaction where a

leaving t-butyl radical leaves H behind, forming  $C_4H_8$ . This is inferred from the concentration independence of pyrolysis rate for TBAs and the product distribution. 3) This data also leads us to postulate a unimolecular reaction producing AsH and  $C_4H_{10}$ . The net effect is the same as for the two-step process described as reaction (1) in this scheme.

TBAs assists TMGa pyrolysis via heterogeneous attack by AsH and AsH<sub>2</sub> radicals formed during TBAs pyrolysis. Similarly, the addition of TBP causes an increase in the TMGa pyrolysis rate by heterogeneous attack of TMGa by adsorbed PH<sub>2</sub> radicals.

The research has proceeded in accord with the objectives contained in the original proposal, with significantly more work performed than originally anticipated.

The results of this project have formed the basis of 13 talks (6 invited) at National and International conferences and 22 completed papers.

Rather than repeating the information contained in the publications and previous reports, the remainder of this report will consist of a brief overview of the accomplishments during the 3rd year with the papers written in the last 12 months attached as an appendix.

## II. RESULTS

### A. SUMMARY OF 3rd YEAR RESEARCH RESULTS

#### 1. TMAs and DMAsH

A definite synergism is observed as the number of similar systems studied mounts. This has led to the study of the pyrolysis of both the methyl-arsenic precursors, described in this section, and the ethyl-arsenic molecules described in section 2, below. In an inert ambient, TMAs pyrolyzes by a largely homogeneous radical fission process. In H<sub>2</sub> and D<sub>2</sub> the process is much faster, due to an additional, hydrogenolysis reaction via a four-center transition state which produces DMAsH and CH<sub>4</sub>, in H<sub>2</sub>, or DMAsD and CH<sub>3</sub>D, in D<sub>2</sub>. The hydrogenolysis reactions continue, eventually producing AsH<sub>3</sub> (or AsD<sub>3</sub> in the deuterium ambient). A key observation for assigning the pyrolysis route to hydrogenolysis is the lack of an effect of toluene additions on the TMAs pyrolysis rate in either He or D<sub>2</sub>: Neither D, nor CH<sub>3</sub> radicals play a role in the pyrolysis process.

The pyrolysis of DMAsH occurs at lower temperatures than for TMAs. The major product in a D<sub>2</sub> ambient is CH<sub>4</sub>. CH<sub>3</sub> radicals

produced by homolysis of DMAsH abstract an H atom from DMAsH to form CH<sub>4</sub>: The ambient has no effect.

The pyrolysis of TMAs is virtually unchanged when TMGa is added to the system in an inert (He) ambient. However, in H<sub>2</sub>, the TMAs pyrolysis rate is increased, due to the creation of H radicals by the TMGa which, in turn, attack TMAs. For DMAs this effect is not observed, since DMAs pyrolyzes at lower temperatures than TMGa. Thus, DMAs slightly assists TMGa pyrolysis by the production of CH<sub>3</sub> radicals. Over a GaAs surface the processes for both TMGa and DMAs pyrolysis become heterogeneous. The data suggest a concerted process producing CH<sub>4</sub> molecules.

## 2. TEAs, DEAs, and MEAs

The homogeneous pyrolysis rate for TEAs in He is independent of ambient, as is the product distribution. The results suggest pyrolysis by sequential elimination of C<sub>2</sub>H<sub>5</sub> radicals. These then recombine and disproportionate to form the products observed: C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>10</sub>. In D<sub>2</sub>, the ethyl radical reacts with the ambient to produce D radicals which attack the parent molecule by abstracting the C<sub>2</sub>H<sub>5</sub> radical, forming C<sub>2</sub>H<sub>5</sub>D. The presence of H atoms bonded to As allows another reaction for DEAs and MEAs, namely the abstraction of the H by the C<sub>2</sub>H<sub>5</sub> radical. This produces a much faster pyrolysis rate for these two precursors as compared with that for TEAs. Even in a deuterium ambient, this produces C<sub>2</sub>H<sub>6</sub>, which becomes the dominant product. These reactions are potentially deleterious for OMVPE, since they remove the H radicals which are relied upon to combine with CH<sub>3</sub> radicals on the growing surface produced by TMGa pyrolysis. Thus, DEAs gives unacceptably high carbon contamination levels in OMVPE-grown GaAs. For MEAs, the concentrations of atomic hydrogen are apparently sufficient to allow material with fairly low carbon concentrations to be grown.

The addition of TMGa assists the pyrolysis of all three ethyl-arsenic precursors studied. By comparing the effects of TMGa and azomethane on the pyrolysis rates and product distributions, the effect of TMGa is deduced to be mainly due to the production of methyl radicals. The CH<sub>3</sub> radicals abstract the C<sub>2</sub>H<sub>5</sub> ligands from TEAs, the C<sub>2</sub>H<sub>5</sub> and H ligands from DEAs, and the H ligands from MEAs.



**B. Summary of Resulting Talks and Papers (for first 2 years of project)**

**TALKS (presented by G.B. Stringfellow unless noted)**

1. "Reaction Mechanisms in the OMVPE Growth of GaAs and InP", OMVPE Workshop, Cape Cod, September 1987. (Presented by N.I. Buchan).
2. "GaAs Growth Using TBAs and TMGa", 4th International Conference on MOVPE, Hakone, Japan, May 1988.
3. "OMVPE Growth of GaAs Using TMGa and TBAs", Electronic Materials Conference, Boulder, June 1988. (Presented by C.A. Larsen).
4. "Reaction Mechanisms in OMVPE Growth of GaAs Determined Using D<sub>2</sub> Labelling Experiments", NATO Workshop on Mechanisms of Reactions of OM Compounds with Surfaces", St. Andrews, Scotland, June 1988. (joint session with European Workshop on MOVPE). (INVITED).
5. "OMVPE for Metastable Alloys and Natural and Artificially Structured Materials", Workshop on Materials Science of Epitaxial Heterostructures, Monterey, Ca, January 9-14, 1989 (INVITED).
6. "Alternative Group V Sources for OMVPE", Materials Research Society Meeting, San Diego, April, 1989 (INVITED).
7. "Reaction Mechanisms for OMVPE Growth of III/V Semiconductors", American Association for Crystal Growth, Western Regional Meeting, Lake Tahoe, California, June 1989 (INVITED).
8. "Chemical Probes in the Study of TBAs and TBP Pyrolysis", 1989 Electronic Materials Conference, Boston, June 1989. (Presented by S.H. Li).
9. "Dimethylarsine: Pyrolysis Mechanism and Use for OMVPE Growth of GaAs", 4th OMVPE Workshop, Monterey, CA, October, 1990 (Presented by S.H. Li).
10. "Alternate Sources and Growth Chemistry for OMVPE and CBE Processes", 2nd International CBE Conference, Houston, November 1989 (INVITED).
11. "Comparative Pyrolysis Study of Ethylarsines", 5th International Conference on MOVPE, Aachen, Germany, June, 1990 (Presented by G.B. Stringfellow).
12. "Mechanistic Study of Organometallic Vapor Phase Epitaxy", 1st International Conference on Epitaxy, Budapest, Hungary, April 1990, (INVITED).
13. "Radical Reactions in Pyrolysis of Monoethylarsine and Diethylarsine", Electronic Materials Conference, Santa Barbara, CA,

June, 1990 (Presented by S.H. Li).

### PAPERS

1. C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, "Reaction Mechanisms in the OMVPE Growth of GaAs", Appl. Phys. Lett. 52 480 (1988).
2. N.I. Buchan, C.A. Larsen, and G.B. Stringfellow, "Mass Spectrometric Studies of TMIn Pyrolysis", J. Crystal Growth 92 591 (1988).
3. N.I. Buchan, C.A. Larsen, and G.B. Stringfellow, "A Mass Spectrometric Study of the Simultaneous Reaction Mechanism of TMIn and PH<sub>3</sub> to Grow InP", J. Crystal Growth 92 605 (1988).
4. C.A. Larsen, N.I. Buchan, S.H. Li, and G.B. Stringfellow, "Decomposition Mechanisms of TBAs", J. Crystal Growth 94 663 (1989).
5. C.A. Larsen, N.I. Buchan, S.H. Li, and G.B. Stringfellow, "Mechanisms of GaAs Growth Using TBAs and TMGa", J. Crystal Growth 94 673 (1989).
6. C.A. Larsen, N.I. Buchan, S.H. Li, and G.B. Stringfellow, "GaAs Growth Using TBAs and TMGa", J. Crystal Growth 93 62 (1988).
7. G.B. Stringfellow, "Reaction Mechanisms in OMVPE Growth of GaAs Determined Using D<sub>2</sub> Labelling Experiments", in Mechanisms of Reactions of Organometallic Compounds with Surfaces, ed. D.J. Cole-Hamilton and J.O. Williams, (Plenum Press, New York, 1989), pp. 117-128.
8. S. H. Li, C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, "Decomposition Mechanisms in the OMVPE Growth of GaP Using TMGa and TBP", Inst. Phys. Conf. Ser. Vol 96, 153 (1989).
9. S.H. Li, C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, "OMVPE Growth Mechanism for GaP Using TBP and TMGa", J. Crystal Growth 96, 906 (1989).
10. S.H. Li, C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, "Pyrolysis of TBP", J. Electron. Mater. 18 457 (1989).
11. S.H. Li, C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, "Study of TBP Pyrolysis Using a Deuterated Source", J. Appl. Phys. 65 5161 (1989).
12. C.A. Larsen, N.I. Buchan, S.H. Li, D.W. Brown, and G.B. Stringfellow, "Decomposition Mechanisms of TMGa", J. Crystal Growth 102 103 (1990).
13. C.A. Larsen, S.H. Li, N.I. Buchan, and G.B. Stringfellow, "Kinetics of Reaction Between TMGa and Arsine", J. Crystal Growth 102 126 (1990).
14. S.H. Li, N.I. Buchan, C.A. Larsen, G.B. Stringfellow, W.P. Kosar, and D.W. Brown, "The Effect of Supplemental t-Butyl

- Radicals on the Pyrolysis Mechanisms of TBAs, TBP, and Ditertiarybutylarsine, *J. Crystal Growth* **98** 309 (1989).
15. S.H. Li, C.A. Larsen, and G.B. Stringfellow, "TMAs Decomposition Mechanisms" *J. Crystal Growth* (submitted).
  16. S.H. Li, C.A. Larsen, C.H. Chen, G.B. Stringfellow, and D.W. Brown, "Dimethylarsine: Pyrolysis Mechanisms and Use for OMVPE Growth", *J. Electron. Mater.* **19** 299 (1990).
  17. G.B. Stringfellow, "Alternate Sources and Growth Chemistry for OMVPE and CBE Processes", *J. Crystal Growth* (Invited Paper and International CBE Conference, to be published).
  18. C.A. Larsen, S.H. Li, and G.B. Stringfellow, "Decomposition Mechanisms of Trimethylantimony and Reactions with Trimethylindium", *J. Crystal Growth* (submitted).
  19. S.H. Li, C.A. Larsen, and G.B. Stringfellow, "Comparative Pyrolysis Study of Ethylarsines", *J. Crystal Growth*, Proceedings of ICMOVPE-5, (accepted).
  20. G.B. Stringfellow, "Mechanistic Study of Organometallic Vapor Phase Epitaxy", Proceedings of 1st International Conference on Epitaxy (Invited Paper, to be published).
  21. S.H. Li, C.A. Larsen, and G.B. Stringfellow, "Monoethylarsine Pyrolysis Mechanisms: Alone and with Trimethylarsine", *J. Crystal Growth* (submitted).
  22. S.H. Li, C.A. Larsen, and G.B. Stringfellow, "Radical Reactions in Pyrolysis of Triethylarsine and Diethylarsine", *J. Crystal Growth* (submitted).

#### C. Students Supported and Graduated

1. N.I. Buchan -- PhD, EE, March 1988  
Thesis Title- "A Spectroscopic Study of Reaction Mechanisms"
2. C.A. Larsen -- PhD, MSE, August 1988  
Thesis Title- "Decomposition Mechanisms of OMVPE"
3. S.H. Li -- PhD, MSE, 1992 (expected).

### III. RESEARCH PLANS

The study of the homogeneous reactions occurring for the precursors alone and in combination, as used for OMVPE, have been nearly completed in the present study. This includes the generation of kinetic data for many of the key reactions.

A logical extension of the present work is to extend the studies to conditions where heterogeneous reactions dominate. Thus, a proposal has

been submitted to allow a study of the group III and group V precursor molecules at low reactor pressures. The pressure range studied will be from atmospheric pressure to the low pressure conditions ( $<10^{-3}$  Torr) where no homogeneous reactions occur, i.e., approaching the chemical beam epitaxy (CBE) regime, where all reactions are heterogeneous. Considerable interest in the alternate group V sources for CBE exists since TBAs and TBP may not require precracking. The required vacuum equipment is in-house. The low pressure studies will be carried-out in a separate, larger reactor tube. Thus, low pressure (in the new system) and atmospheric pressure (in the old system) experiments can both be performed in the modified apparatus. Thus, pyrolysis and growth studies for new precursors can be carried out as they become available.

**APPENDIX A: PREPRINTS AND REPRINTS OF PAPERS RESULTING  
FROM THE LAST 12 MONTHS OF AFOSR SUPPORT**